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according to embodiments of the present invention exhibited stable cycling. The hybrid anode comprised a graphite felt electrode connected in parallel with a Li foil, wherein the graphite felt and the Li were separated by a Celgard porous separator. In some embodiments, a separator can provide improved protection to the SEI layer. The graphite felt electrode can function as the intercalation anode material to minimize lithium metal deposition. Meanwhile, the graphite felt is electrically connected to the Li foil via a stainless steel mesh to harvest the same redox potential of the Li/Li⁺ redox couple.

FIGS. 10A and 10B show the cycling efficiencies, and the volumetric specific capacities and discharge energy density of the 0.8 M Li|Fc1N112-TFSI flow cell over 18 cycles at 1.5 mA cm⁻². A relatively stable EE of 76% was achieved despite a gradual increase in the CE (85% to 91%) and drop in the VE (87% to 83%). The flow cell exhibited moderate capacity retention. A volumetric discharge energy density of ~53 Wh L⁻¹ was delivered in the initial cycles, which is about twice of that of practical VRB systems (~25 Wh L⁻¹). Compared to the 0.1 M Fc1N112-TFSI situation, the CE at the 0.8 M catholyte concentration is lower due to longer charge/discharge durations yielding more self-discharge, and the VE is also lower due to decreased conductivity of the catholyte solution.

Without any additive, a 0.1 M Li|Fc1N112-TFSI flow cell could only operate at current densities below approximately 0.25 mA cm⁻². Under similar flow cell test conditions, vinyl carbonate (VC) and/or FEC at 2 wt % content can stabilize the SEI up to 2.5 mA cm⁻² and 5.5 mA cm⁻², respectively. However, at higher catholyte concentrations, the additives were not able to meet the increased demand for SEI stabilization due to extended lithium deposition. Flow cell tests were not successful even at 0.2 M Fc1N112-TFSI concentration under the same testing condition using merely a Li anode. Embodiments of the present invention, which have a hybrid anode comprising first and second electrodes (e.g., graphite felt and Li metal, respectively) connected in parallel can result in retardation of dendrite formation and proliferation without sacrificing any of the cell potential.

The anode side can be engineered to have static Fc1N112 electrolyte or flowing Fc1N112 electrolyte.

While a number of embodiments of the present invention have been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims, therefore, are intended to cover all such changes and modifications as they fall within the true spirit and scope of the invention.

We claim:

1. A redox flow battery (RFB) having a first half cell comprising a first redox couple dissolved in a solution or contained in a suspension, a second half cell comprising a solid hybrid electrode, and a separator or membrane between the first and second half cells, the solid hybrid electrode comprising a first electrode connected to a second electrode, thereby resulting in an equipotential between the first and second electrodes, wherein the first electrode comprises a carbon electrode as a conductive solid material and the second electrode comprises a lithium as a solid electroactive metal.

2. The RFB of claim 1, wherein the carbon electrode comprises a carbonaceous material selected from the group consisting of graphite, hard carbon, carbon black, carbon fibers, carbon nanotubes, graphite felt, graphene, and combinations thereof.

3. The RFB of claim 1, wherein the second electrode further comprises an electroactive metal selected from the group consisting of Na, K, Zn, Si, Mg, Ca, Al, Sn, Fe, and combinations thereof.

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4. The RFB of claim 1, wherein the first redox couple comprises a redox active organic compound.

5. The RFB of claim 4, wherein the redox active organic compound is selected from the group consisting of TEMPO, anthraquinones, DBBB, sulfides, disulfides, polysulfides, nitroxyl radicals, galvinoxyl radicals, carbonyl compounds, quinones and quinone derivatives, TEMPO, metallocenes ferrocenes, carbazoles, tertiary amines, 2,5-di-tert-butyl-1,4-dialkoxybenzenes, quinoxalines, phthalocyanines, porphyrins, pyrazines, and combinations thereof.

6. The RFB of claim 1, wherein the first redox couple comprises a redox active inorganic compound.

7. The RFB of claim 6, wherein the redox active inorganic compound is selected from the group consisting of sulfur and sulfur compounds, selenium and selenium compounds, iodides and polyiodides, bromides and polybromides, chlorides and polychlorides, and combinations thereof.

8. The RFB of claim 6, wherein the redox active inorganic compound comprises Li_xS_y, wherein x is from 0 to 4, and y is from 1 to 8.

9. The RFB of claim 1, wherein the first redox couple comprises a redox active organometallic compound.

10. The RFB of claim 9, wherein the redox active organometallic compound comprises a ferrocene compound.

11. The RFB of claim 1, wherein the first redox couple has a concentration greater than 0.1 M in a liquid solvent.

12. The RFB of claim 1, wherein the first redox couple has a concentration greater than or equal to 0.5 M in a liquid solvent.

13. The RFB of claim 1, further comprising a hybrid electrode separator between the first electrode and the second electrode.

14. The RFB of claim 1, wherein the second electrode is in direct contact with the first electrode.

15. The RFB of claim 1, wherein the first electrode further comprises metalated carbon during charging and discharging of the redox flow battery.

16. The RFB of claim 1, wherein the first electrode further comprises metal ions intercalated therein, deposited thereon, or both.

17. The RFB of claim 16, wherein the metal ions comprise lithium ions.

18. The RFB of claim 1, further comprising a reservoir containing a supply of the first redox couple dissolved in the solution or contained in the suspension, the reservoir connected to the first half cell via a conduit and a flow regulator.

19. The RFB of claim 1, wherein the second half cell further comprises a fluid circulator to induce flow in an electrolyte in the second half cell.

20. A redox flow battery (RFB) having a first half cell comprising a first redox couple dissolved in a solution or contained in a suspension at a concentration greater than 0.1 M, a second half cell comprising a solid hybrid electrode, and a separator or membrane between the first and second half cells, the hybrid electrode comprising a first electrode connected to a second electrode, thereby resulting in an equipotential between the first and second electrodes, wherein the first electrode comprises a carbon electrode as a conductive solid material and the second electrode comprises a lithium as an electroactive metal.

21. A method of operating an RFB having a first half cell comprising a first redox couple dissolved in a solution or contained in a suspension, a second half cell comprising a solid hybrid electrode, and a separator or membrane between the first and second half cells, the method comprising the step of operating a first electrode and a second electrode at an equipotential, wherein the hybrid electrode comprises the